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PS 0043 18 January 2002 (18.01.2002) AU(71) Applicant (for all designated States except US): CAST
CENTRE PTY LTD [AU/AU]: Cooper Road, St Lucia,
QLD 4067 (AU).

(72) Inventors; and

(75) Inventors/Applicants (for US only): QIAN, Ma

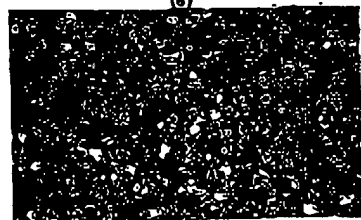
[AU/AU]: 17 Hindmarsh Place, Westlake, QLD 4074
(AU). STJOHN, David [AU/AU]: 26 Gladstone Street,
Indooroopilly, QLD 4068 (AU). FROST, Malcolm,
Timothy [AU/AU]: 104 Creekside Street, Kenmore, QLD
4069 (AU).(74) Agent: GRIFFITH HACK; Level 10, 167 Eagle Street,
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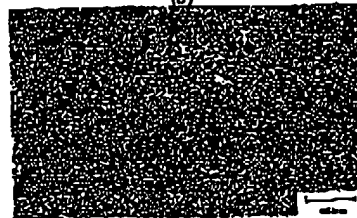
(54) Title: MAGNESIUM-ZIRCONIUM ALLOYING



(a)



(b)



(c)

Optical micrographs showing the grain refining ability of pretreated sponge when added to pure magnesium at 680 °C. All micrographs are of the same magnification. (a) Pure magnesium, (b) after adding 1 wt% sponge, followed by 20 minutes manual stirring, and (c) after a further 10 minutes stirring.

(57) Abstract: Zirconium sponge can be chemically depassivated by treatment with hydrofluoric acid to improve the ability of molten magnesium/magnesium alloy to dissolve zirconium from the treated zirconium sponge and to form a melt containing substantially evenly distributed particles of zirconium.

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DT04 Rec'd PCT/PTO 16 JUL 2004**MAGNESIUM-ZIRCONIUM ALLOYING**FIELD OF THE INVENTION

- 5 The present invention relates to the addition of zirconium to pure magnesium or magnesium alloys and to the preparation of magnesium-zirconium (Mg-Zr) alloys, including Mg-Zr master alloys.

10 BACKGROUND TO THE INVENTION

- Zirconium is a potent grain refiner for magnesium alloys which contain negligible amounts of elements with which zirconium forms stable compounds, such as Al, Si, Fe, Ni, Co, Sn and Sb. Zirconium additions of about 1% by weight to such magnesium alloys can readily cause the grain size to decrease by 80% or more under normal cooling rates. The exceptional grain refining ability makes zirconium an important alloying element for magnesium alloys that are not based on alloying with Al and Si. For example, zirconium containing Mg-RE-Zn alloys such as EZ33 (Mg-3.3RE-2.7Zn-0.6Zr) and ZE41 (Mg-1.2RE-4.2Zn-0.7Zr) offer a specific combination of elevated temperature and room temperature properties which are not achievable with the Mg-Al-Zn alloys.

- The solubility of zirconium in molten pure magnesium is approximately 0.6%, which slightly increases with increasing melt temperature. It has been reported that the most characteristic feature of the microstructure of a magnesium alloy that contains more than a few tenths per cent soluble zirconium is the zirconium-rich cores that exist in most of the magnesium grains. These zirconium-rich cores are believed to be the products of peritectic solidification. In order to achieve excellent grain refinement in commercial production, it is desirable to dissolve the full zirconium content (ie, about 0.6%) in a

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magnesium melt.

Over the decades various approaches to introducing zirconium into molten magnesium have been explored,

5 including:

- (a) alloying with different forms of zirconium metal;
- (b) alloying with zirconium sponge;
- (c) alloying with Zn-Zr master alloys;
- 10 (d) alloying with ZrO_2 ;
- (e) alloying with various zirconium halides or complex halides or a mixture of halides and/or complex halides with different salts such as NaCl, KCl, $BaCl_2$, NaF, KF, etc; and
- 15 (f) alloying with Mg-Zr master alloys.

The advantages and disadvantages of each of these approaches have been discussed in detail by Saunders and Strieter (W. P. Saunders and F. P. Strieter, "Alloying
20 Zirconium to Magnesium", Transactions of the American Foundrymen's Society, 1952, Vol. 60, pp. 581-594) and Emley (E. F. Emley, "Principles of Magnesium Technology", Pergamon Press, Oxford, 1966, pp. 127-155). Since about 1960, only Mg-Zr master alloys have been in
25 widespread commercial use as sources of zirconium for alloying with magnesium. These Zr-rich Mg-Zr master alloys are made by chemical reduction by magnesium of salt mixtures based on zirconium fluorides or zirconium chlorides. Both types of master alloy are essentially the
30 same and contain about one third their weight of zirconium. One of them, developed by Magnesium Elektron Ltd (MEL) in about 1945 via chemical reduction of a complex zirconium fluoride with molten magnesium, has been long known as Zirmax (trade mark). A similar type of Mg-Zr
35 master alloy was developed in the United States based on a chloride salt reduction process.

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Zirmax type master alloys remain the primary zirconium alloying material used for the commercial production of zirconium-containing magnesium alloys. Zirmax contains approximately 33% zirconium and 67% magnesium and most of the zirconium is present as various sizes of zirconium particles (mostly in the range of submicron to 10 μ m) in a magnesium matrix.

Prior to Zirmax type master alloys becoming the standard source of zirconium for zirconium-containing magnesium alloys, alloying with various forms of zirconium metal were investigated.

Sauerwald published work on alloying zirconium metal powder to magnesium in 1947 (V. F. Sauerwald, "Das Zustandsdiagramm Magnesium-Zirkonium", Zeitschrift für anorganische Chemie, 1947, Band 255, pp. 212-220). He added 5 wt% zirconium metal powder to magnesium under an argon atmosphere at various temperatures between 680 and 1100°C. Soluble zirconium contents exceeding 0.5 wt% (samples were digested in HCl acids) were obtained at all temperatures tested. In the same year, Ball reported work (C. J. P. Ball, "Metallurgia", 1947, Vol. 35, pp. 125-129; 211) stating that metallic zirconium dissolves in magnesium under an argon atmosphere at 900-1100 °C but that it was a difficult and costly process. Operating at such temperatures is not commercially feasible in view of vaporisation of magnesium. Emley reported in 1948 (E. F. Emley, "Discussions of the Faraday Society", 1948-49, Vol. 47, No. 4, pp. 219) that as zirconium metal powder is expensive and highly inflammable, it is natural to consider the possibility of alloying by a reducible zirconium compound.

In 1952, Saunders and Strieter reported their investigations in which different forms of metallic zirconium, (ie, zirconium sponge, fused zirconium, iodide-

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decomposed ductile zirconium, and zirconium powder) were investigated as zirconium alloying materials for magnesium at 760 °C (1400 F). The fused lump zirconium was added as 6.35-mm (¼-in.) pieces in a small steel ladle and stirred in the ladle with a steel rod. No apparent solution had occurred after 30 minutes of stirring. Analysis of the melt showed a result of 0.03% soluble zirconium content with 1% zirconium addition. Iodide zirconium sheet, rolled to about 127 - 254µm (0.005-0.010 in.) and cut into 6.35mm (¼-in.) squares was added in a manner similar to that used for the fused lump zirconium. It was stirred for several minutes in the ladle. It was found that after 65 minutes of holding at temperature, the resultant soluble zirconium content merely reached 0.1% with 1% zirconium addition.

The use of zirconium powder was evaluated by adding it in various ways because zirconium powder is pyrophoric and some means of protecting the powder from oxidation had to be applied. Zirconium powder was pelleted with various binders, zirconium powder was enclosed in tight magnesium capsules, zirconium powder was compacted with magnesium powder, and zirconium powder was used in the form of sintered zirconium powder briquettes. In general, with 3% zirconium addition to a Mg-5Zn melt, the resultant zirconium content was reported as varying between 0.7 and 0.85%. The solubility of zirconium in magnesium is influenced by the presence of a third element. It was reported that with the presence of Zn at a level around 3-4%, the solubility of Zr in magnesium could be increased from 0.6% to slightly over 0.7% and 5% zinc increases the solubility of Zr in magnesium to about 0.8%.

According to Saunders and Strieter, of the various metallic forms of zirconium tested, alloying with zirconium sponge demonstrated the most promising results.

The zirconium sponge used was made by the Kroll process

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- ((a) zirconium tetrachloride is produced by the action of chlorine and carbon on a zirconium oxide such as baddeleyite (ZrO_2) or zircon ($ZrSiO_4$)
- $ZrO_2 + 2Cl_2 + 2C (900^\circ C) \rightarrow ZrCl_4 + 2CO$, or
- 5 $ZrSiO_4 + 4Cl_2 + 4C (900^\circ C) \rightarrow ZrCl_4 + SiCl_4 + 4CO$;
- (b) the resultant zirconium tetrachloride is separated from iron trichloride (from iron impurities) and silicon tetrachloride (if present) by fractional distillation; and
- 10 (c) the purified zirconium tetrachloride is reduced by reaction with molten magnesium under argon to produce "zirconium sponge" - $ZrCl_4 + 2Mg (1100^\circ C) \rightarrow Zr + 2MgCl_2$).

In their experiments, the sponge was essentially ground with the average size being reduced to about $12.7 \mu m$ or

15 0.0005 in. The results showed that zirconium sponge produced a soluble zirconium content of about 0.62-0.66% in Mg-5Zn alloys with 3% zirconium addition after 3-4 minutes stirring. With 1% zirconium sponge addition, soluble zirconium contents in the range of 0.32 to 0.52%

20 were achieved. Furthermore, the authors found that the alloying efficiency decreased when the sponge fragments were decreased in size because when the particles became finer powder, the material burned up before it could be submerged beneath the melt. Therefore, some means of

25 protecting the powder from oxidation had to be applied.

Despite the excellent alloying results demonstrated by the work of Saunders and Strieter with Kroll process zirconium sponge, alloying zirconium sponge to magnesium was in

30 general limited to laboratory scales. As realised and pointed out by Saunders and Strieter, "an important disadvantage in the commercial use of sponge in the magnesium alloying field is the rather laborious effort required to alloy the material". This laborious effort

35 apparently refers to the grinding process because the alloying process employed, ie, 3-4 minutes of stirring, was plainly simple. In addition, the unavoidable

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contamination problem arising from the grinding process is another important disadvantage in the commercial use of zirconium sponge.

- 5 In *Principles of Magnesium Technology*, Emley similarly commented about alloying zirconium metal to magnesium: "pure zirconium metal is expensive by any route and very inflammable in powder form, and for these reasons, coupled with the ease with which it becomes contaminated with oxygen, hydrogen and nitrogen, the approach via zirconium metal is not obviously the best".

- 15 Experiments have indicated that in commercial production of magnesium alloys, when Zirmax is dissolved into a magnesium melt at commercially useful addition rates, undissolved zirconium particles can be readily observed in the microstructure of the magnesium alloy produced (Ma Qian, L. Zheng, D. Graham, D. H. StJohn and M. T. Frost, "Settling of undissolved zirconium particles in pure magnesium melts", *Journal of Light Metals*, 2001, Vol. 1, No.3, pp. 157-165 and Y. Tamura, N. Kono, T. Motegi and E. Sato, "Grain refining mechanism and casting structure of Mg-Zr alloys", *Journal of Japan Institute of Light Metals*, 1998, Vol. 48, No. 4, pp. 185-189). Many of these residual (undissolved) zirconium particles have an average size of around 5 μm .

- The density of zirconium is 6.5gcm^{-3} whereas the density of molten magnesium is 1.6gcm^{-3} . Zirconium particles therefore have a strong tendency to settle in a magnesium melt unless stirred vigorously. The larger the particle, the faster it settles to the bottom of the melt. For example, a 15-micron zirconium particle has been found to fall at approximately 40 mm/min to the bottom of a magnesium melt at 780 °C and is therefore difficult to maintain such particles suspended in a melt at this temperature. By contrast, when the particle size is

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smaller than 3 microns, it can be readily suspended in a magnesium melt at the same temperature.

Chambers Science and Technology Dictionary (1991) defines "passivity" as "Lack of response of metal or mineral surface to chemical attack such as would take place with a clean, newly exposed surface. Due to various causes, including insoluble film produced by ageing, oxidation, or contamination; run-down of surface energy at discontinuity lattices; adsorbed layers..." Throughout this specification, the terms "depassivate", "depassivated" and "depassivating" are to be understood to have meanings derived from the foregoing definition of "passivity".

15 SUMMARY OF THE INVENTION

In a first aspect, the present invention provides a method for treating zirconium metal, the method comprising chemically depassivating the zirconium metal. The zirconium metal is preferably zirconium sponge with the method forming treated zirconium sponge. The zirconium sponge may be chemically depassivated by treatment with a source of fluoride ions. The source of fluoride ions may be hydrofluoric acid. The source of fluoride ions may be a mixture of hydrofluoric acid and nitric acid.

The hydrofluoric acid preferably has a concentration between 0.10% and 50.0%, more preferably between 0.50% and 5.0%, and most preferably between 1.5% and 2.5%, with the acid concentrations calculated as shown later in this specification. These acid concentration ranges correspond respectively to 0.05 - 50.0 molar, 0.25 - 2.63 molar and 0.76 - 1.28 molar, which may be rounded to 0.05 - 50.0 molar, 0.25 - 3.0 molar and 0.75 - 1.5 molar.

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In a second aspect, the present invention provides a method for treating zirconium sponge, the method comprising treating the zirconium sponge with a solution containing fluoride ions to form treated zirconium sponge.

5

The zirconium sponge is preferably a porous agglomerate of zirconium grains. Preferably, the sponge is formed by the Kroll process.

- 10 Preferably, the sponge comprises zirconium with only incidental impurities. Hafnium is a common impurity in zirconium. In contrast, Fe, Ni, Al, Si, C, Co, Sn and Sb are undesirable as they are alloying inhibiting and their total concentration is preferably less than 1% and, more
15 preferably less than 0.5%.

- Preferably, the zirconium sponge is in the physical form of small particles and each particle has a porous structure. Preferably, these zirconium sponge particles
20 have the following properties:
- the particles have an average size between 0.1 to 10 mm, more preferably between 0.5 and 5mm
 - the particles have a minimum size of 0.5mm, more preferably 1mm, and a maximum size of
25 10mm, more preferably 5mm
 - density of sponge = $5.2-6.3\text{g/cm}^3$, more preferably $5.5-5.8\text{g/cm}^3$
 - porosity of sponge ($1 - \text{density of sponge/density of solid zirconium}$) = $0.08-0.2$, more preferably $0.11-0.15$.
30
 - the void sizes on a polished transverse section of each zirconium sponge particle are in general between 5 and 60 μm .

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In a third aspect, the present invention provides treated zirconium sponge prepared by a method according to the first or second aspects of the present invention.

- 5 As compared with untreated (as received) zirconium sponge, treatment of zirconium sponge in accordance with the present invention has been found to improve the ability of molten magnesium/magnesium alloy to dissolve zirconium and to form a melt containing substantially evenly distributed
10 particles of zirconium.

In a fourth aspect, the present invention provides zirconium sponge comprising an agglomerate of zirconium particles and having a surface layer containing fluorine
15 containing compounds at least partially coating at least some of the particles. The fluorine containing compounds are preferably zirconium fluoride compounds and may be compounds of the formula $Zr_xF_y.nH_2O$.

- 20 In a fifth aspect, the present invention provides a method of manufacturing a magnesium-zirconium master alloy, the method comprising the steps of:

- (a) mixing treated zirconium sponge according to the third aspect of the present invention or
25 zirconium sponge according to the fourth aspect of the present invention with molten magnesium/magnesium alloy to form a magnesium-zirconium melt containing dissolved zirconium and zirconium particles; and
30 (b) casting the magnesium-zirconium melt to solidify as the magnesium-zirconium master alloy.

Preferably, the sponge is mixed with the molten magnesium/magnesium alloy by stirring.

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In a sixth aspect, the present invention provides a magnesium-zirconium master alloy manufactured by a method according to the fifth aspect of the present invention. Preferably, the master alloy contains 10%-50%, more preferably 20%-40%, zirconium in magnesium/magnesium alloy. Preferably, at least 90% of the zirconium particles in the master alloy are sized less than 5 μ m, more preferably less than 3 μ m. Preferably, the average particle size is less than 5 μ m.

10

In a seventh aspect, the present invention provides a magnesium-zirconium master alloy containing dissolved zirconium and zirconium particles in the substantial absence of halide inclusions wherein 90% of the zirconium particles are sized less than 5 μ m, preferably less than 3 μ m.

15

Preferably, the master alloy is cast as ingots, which term is to be understood to include briquettes, pellets and the like.

20

In an eighth aspect, the present invention provides a method of adding zirconium as an alloying element to molten magnesium/magnesium alloy, the method comprising mixing treated zirconium sponge according to the third aspect of the present invention or zirconium sponge according to the fourth aspect of the present invention with the magnesium/magnesium alloy.

25

In a ninth aspect, the present invention provides a method of adding zirconium as an alloying element to molten magnesium/magnesium alloy, the method comprising mixing a magnesium-zirconium master alloy according to the sixth or

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seventh aspects of the present invention with the molten magnesium/magnesium alloy.

5 Preferably, the amount of zirconium added to the molten magnesium/magnesium alloy is greater than that required to saturate the magnesium/magnesium alloy with zirconium at the temperature of the melt.

10 In a tenth aspect, the present invention provides a magnesium alloy containing zirconium prepared by a method according to the eighth or ninth aspects of the present invention.

BRIEF DESCRIPTION OF THE FIGURES

15 In order that the invention may be more fully understood there will now be described, by way of example only, preferred embodiments and other elements of the present invention with reference to the below mentioned
20 accompanying illustrations.

Figures 1(a)-(c) are micrographs illustrating the grain refining ability of as-received and untreated zirconium sponge when added to pure magnesium at 730 °C. All three
25 micrographs are of the same magnification. Figure 1(a) is pure magnesium, Figure 1(b) is after addition of 1wt% untreated zirconium sponge followed by 30 minutes of manual stirring, and Figure 1(c) is after addition of a further 1wt% untreated zirconium sponge followed by a
30 further 30 minutes of manual stirring.

Figures 2(a)-(c) are micrographs illustrating the grain refining ability of as-received and untreated zirconium sponge when added to pure magnesium at 780 °C. All three
35 micrographs are of the same magnification as in Figures 1(a)-(c). Figure 2(a) is pure magnesium, Figure 2(b) is after addition of 1wt% untreated zirconium sponge followed

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by two minutes of manual stirring and then 30 minutes holding at 780°C. and Figure 2(c) is after a further holding of 210 minutes at 780°C.

- 5 Figures 3(a)-(c) are micrographs illustrating the grain refining ability of treated zirconium sponge of the present invention when added to pure magnesium at 680 °C. All three micrographs are of the same magnification as in the previous figures. Figure 3(a) is pure magnesium,
- 10 Figure 3(b) is after addition of 1 wt% treated zirconium sponge followed by 20 minutes of manual stirring, and Figure 3(c) is after a further 10 minutes of manual stirring.
- 15 Figures 4(a)-(c) are micrographs illustrating the grain refining ability of treated zirconium sponge of the present invention when added to pure magnesium at 730 °C. All three micrographs are of the same magnification as in the previous figures. Figure 4(a) is pure magnesium,
- 20 Figure 4(b) is after addition of 1 wt% treated zirconium sponge followed by 30 minutes manual stirring, and Figure 4(c) is after 30 minutes of holding and then a further two minutes of manual stirring.
- 25 Figures 5(a)-(c) are micrographs illustrating the grain refining ability of treated zirconium sponge of the present invention when added to pure magnesium at 800 °C. All micrographs are of the same magnification as in the previous figures. Figure 5(a) is pure magnesium, Figure
- 30 5(b) is after addition of 1 wt% treated zirconium sponge followed by 30 minutes of manual stirring, and Figure 5(c) is after 30 minutes of holding and then a further two minutes of manual stirring.
- 35 Figure 6 is a photograph showing the physical form of untreated (as received) zirconium sponge particles as used in one embodiment of the present invention.

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Figure 7 is a micrograph showing a view of a typical microstructure of the zirconium sponge particles shown in Figure 6 after treatment in accordance with the present invention.

Figure 8 is a micrograph showing a view of an alternative microstructure for the zirconium sponge particles shown in Figure 6 after treatment in accordance with the present invention.

Figure 9 is a schematic diagram illustrating a method of adding treated zirconium sponge to molten magnesium.

Figures 10 and 11 show typical views of the microstructure of an ingot of master alloy produced according to the present invention.

Figures 12 and 13 show typical views of commercially available Zirmax master alloy.

Figures 14 and 15 show typical views of the microstructure of an ingot of master alloy produced according to the present invention.

Figure 16 is a micrograph showing reaction products left on zirconium sponge particles after treatment in accordance with the present invention.

30 EXAMPLES

Comparative Trial

35 An untreated (as received) zirconium sponge in the physical form of zirconium sponge particles of size 1-10 mm diameter was selected. The major impurity in the sponge was hafnium. The impurity concentrations were:

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	Hf	= 0.8% approx
	Fe+Cr	= 0.1%
	C	= 0.004%
	H	= 0.001%
5	N	= 0.002%

The sponge was added, without treatment in accordance with the present invention, to two samples of molten magnesium at 730 and 780 °C respectively. Cone samples ($\phi 30 \times \phi 20 \times 25$ mm) were collected at different times and examination showed little evidence of grain refinement (see Fig. 1 and Fig. 2) even when the melt was held at 780°C for 2 to 6 hours. Wet chemical analyses of the soluble zirconium contents in the samples using 15% HCl acid showed negligible zirconium contents ($< 0.05\%$).

Preparation of Treated Zirconium Sponge

Zirconium sponge identical to that used in the Comparative Trial above was first immersed in an acid solution which was prepared in the following manner:
45ml of concentrated nitric acid (68.5%-69.5%) and 45ml of concentrated hydrofluoric acid (50%) were combined and diluted in water to a total of 1000ml. This gave an acid solution of approximately 3% HNO_3 and 2% HF, which equates to approximately 1.1 molar HF and 0.5 molar HNO_3 .

The zirconium sponge was left in this acid solution for 5 minutes. Bubbling was observed which indicated that the acid had probably at least partially removed the ZrO_2 layer and was dissolving some of the zirconium metal underneath. After removal from the acid solution the zirconium sponge was rinsed in ethanol and dried under heating lamps at approximately 50°C for 60 minutes. Water was also found to be a suitable rinsing agent.

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The treated zirconium sponge used in preparing the alloys depicted in Figures 3-5 was prepared by immersing zirconium sponge identical to that used in the Comparative Trial in a HF solution for 5 minutes followed by rinsing in water and drying. The HF solution was prepared by diluting 45ml of concentrated HF(50%) in water to a total of 1,000mls to give approximately 2.25% HF which equates to approximately 1 molar HF.

- 10 An alternative acid solution which was successfully used was 0.07-0.25% HF. This is a very dilute HF acid solution and is readily handled.

- 15 Treated zirconium sponge was prepared by immersing zirconium sponge identical to that used in the Comparative Trial in a 2% HF solution for 4 minutes followed by rinsing in water and drying. The reaction products of the treatment are evident as the white phases on the sponge particles in Figure 16.

- 20 Although it is thought that successful treatment involves the dissolution or some physical removal of oxide from the Zr surface, we do not wish to be bound by any theory as to why such treatment is effective.

- 25 XPS analyses of treated and untreated sponge particles gave the results set out in Table 1 below. The treated particles were immersed in 0.5% HF solution for 4 minutes, rinsed with water and dried. For each analysis given, information was collected from a depth of 5 nanometers or 10 atomic layers on the surfaces of six different large particles.
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Table 1 XPS analyses of treated and untreated sponge particles

Sponge Particles	Surface composition in atom percentage								
	C	O	Zr	Fe	Si	F	Cl	Mg	Hf
Untreated	30.5	49.2	16.2	1.1	3.0	0	0	0	0
Treated particles (black)	10.3	43.3	14.9	1.3	2.3	27.8	0	0	0
Treated particles (grey)	26.0	41.1	15.6	1.1	1.7	27.4	0	0	0

According to the energy level detected for each element, O is present in the form of ZrO_2 in all three cases studied and the detected F in the treated particles is present in the form of $Zr_xF_y \cdot nH_2O$, such as ZrF_4 .

In all of the experiments conducted it was observed that the weight of the sponge particles decreased with increasing treatment time in the acid solution until all of the particles disappeared or the HF was consumed.

Although we did not wish to be bound by any theory, it is presently thought that the mechanism is that the treatment results in the oxide film on each sponge particle being partially or totally removed and a layer of reaction products (possibly $Zr_xF_y \cdot nH_2O$), either continuous or discontinuous, being formed on the particles. Owing to the formation of the $Zr_xF_y \cdot nH_2O$ patches or coating on the sponge particles, oxidation of zirconium beneath these patches or the coating would be prevented after treatment. It is thought that the patches then dissolve into molten magnesium, leaving parts of the zirconium surface exposed to the molten magnesium thereby providing fresh contact sites for the molten magnesium. BSE images have revealed that there are many tiny channels in each sponge particle

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which provides an explanation for the disintegration of the sponge particles.

5 The above proposed mechanism is offered only as a possible explanation of the experimental results and there could be other mechanism(s). The present invention may incorporate but is not to be considered limited by the mechanism described.

10 Preparation of Magnesium-Zirconium Alloy

A hole was machined into a small piece of magnesium ingot and the required pieces of treated zirconium sponge were placed into the hole as illustrated in Figure 9. This
15 piece of ingot was then quickly submerged below the magnesium melt surface. This allowed the treated zirconium sponge to be introduced directly to the melt without the possibility of it remaining on the surface of the melt. The approach avoided the treated sponge being trapped in
20 the dross and avoided the treated sponge not being wetted by the melt. The sponge could be added to the melt in various other ways, such as by adding a compact of sponge particles, providing that it is successfully introduced below the surface.

25 It has been found that, alternatively, the zirconium sponge particles can be directly added to the melt under certain circumstances. An example is if the magnesium melt surface is protected with cover gas such as 1% SF₆
30 (balance: 49.5% CO₂ and 49.5% dry air), and the concentration of oxygen above the surface of the magnesium melt is therefore very low, the sponge particles can be successfully added directly providing it is done quickly. For example, the zirconium sponge particles can be added
35 at a height of 800 mm away from the melt surface through a steel funnel, where the bottom of the funnel is placed just above the melt surface. This allows the sponge

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particles to quickly get into the melt without being oxidised. This has been proved to be a very convenient way of adding small (< 5mm) zirconium sponge particles to magnesium melts.

5

After addition of the treated zirconium sponge at a rate of 1% by weight, the melt was left for a couple of minutes to reheat to the correct temperature and was then stirred for 30 minutes. Three temperatures were used: 680°C, 730°C and 800°C. Cone samples were collected at different times after the addition of the treated zirconium sponge.

10

Figures 3 to 5 show a typical view of the grain structures achieved from the three tests, respectively.

15

Results of wet chemical analysis are summarised in Table 2 which lists the wet chemical analysis results of soluble zirconium contents in samples taken from all three alloying tests.

20

Table 2 Soluble and total zirconium contents of samples by wet chemical analysis (%)

	Alloying temperatures					
	680°C		730°C		800°C	
	1 wt% sponge addition		1 wt% sponge addition		1 wt% sponge addition	
	Soluble*	Total**	Soluble	Total	Soluble	Total
Before addition	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
30 min. stirring	0.48	0.93	0.56	0.76	0.54	0.92
A further 30 min. holding			0.56	0.85	0.56	0.66
Restirring for 2 min.			0.56	0.97	0.57	0.74

* Soluble: 15% HCl

** Total: 50% HCl + 6% HF

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As can be seen, the soluble zirconium content reached 0.56% at both 730°C and 800°C after 30 min. stirring. This is very close to the solubility limit of zirconium, ie, 0.6 wt%, in molten pure magnesium. The soluble zirconium contents achievable by addition of the same amount of zirconium from Zirmax master alloy have been reported as generally less than 0.5% and are typically around 0.4% at 720°C - see Y. Tamura, N. Kono, T. Motegi and E. Sato, "Grain refining mechanism and casting structure of Mg-Zr alloys", Journal of Japan Institute of Light Metals, 1998, Vol. 48, No. 4, pp. 185-189. The use of pretreated zirconium sponge showed a better recovery compared with the use of the Zirmax master alloy.

15 Stability of Treated Zirconium Sponge

A solution of 0.4% HF was prepared by adding 40ml of 10% HF to 960ml of water. Zirconium sponge identical to that used in the Comparative Trial was immersed in the 0.4% HF at room temperature for 5 minutes and then rinsed in water and dried. The dry treated zirconium sponge were stored in a plastic bag.

After four weeks of storage, 300g of the treated zirconium sponge particles were added to 30kg of pure magnesium at 680°C and stirred. Chill bar samples (25mm in diameter) were cast prior to addition of the treated zirconium sponge particles, after 30 minutes of stirring, and after 60 minutes of stirring.

Very good grain refinement was achieved after 30 minutes of stirring. The soluble and total zirconium contents were 0.38% and 0.69% respectively after 30 minutes of stirring which increased to 0.42% and 0.81% respectively after 60 minutes of stirring.

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Preparation of Magnesium-Zirconium Master Alloy

A total of 150g of treated zirconium sponge particles in the size range of approximately 1-3mm was added to a 550g magnesium melt at 730°C. The nominal addition of zirconium was approximately 25 wt%. These zirconium particles were added in two batches. Stirring was applied throughout the whole alloying process. The melt was cast into a steel ingot mould after 60 minutes of stirring.

Figures 7 and 8 show typical views of the microstructure of the treated zirconium sponge. Owing to the gradual dissolution of the porous structure, each zirconium sponge particle will eventually be disintegrated into many fine zirconium particles sized about 2-3µm. Production of a suspension of fine zirconium particles in the melt is enhanced by maintaining gentle stirring throughout.

The magnesium-zirconium melt produced as described above can be cast into different moulds, preferably into chill moulds. Preferably the height of each ingot is not much greater than 500 mm unless the mould employed has an excellent chilling effect. Where possible, a low casting temperature such as 680 °C or lower is preferred. Cover gas should be used during casting.

Figures 10 and 11 show typical views of the microstructure of the ingot produced according to the above description with 25% zirconium addition. The white phases are zirconium particles. Figures 12 and 13 show typical views of MEL's Zirmax master alloy. As can be seen, the zirconium particles present in the master alloy of the present invention are in general smaller than those present in Zirmax. Small zirconium particles are always highly preferred as discussed earlier.

A magnesium-zirconium master alloy containing

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approximately 50wt% zirconium was prepared by adding 440g of treated zirconium sponge particles to 440g of molten magnesium at 700°C with slow manual stirring for 90 minutes. Figures 14 and 15 are typical views of the microstructure of an ingot cast on completion of the stirring in which the grey particles are zirconium and the white phases are magnesium.

10 Preparation of Magnesium-Zirconium Alloy from Magnesium-Zirconium Master Alloy

Magnesium-zirconium master alloy containing approximately 25wt% zirconium (prepared in accordance with the present invention) was added to a crucible containing 30kg of molten magnesium at 730°C. The master alloy was preheated to approximately 175°C prior to addition to the crucible and sufficient master alloy was added to give a zirconium addition of approximately 1wt%.

20 Following addition of the master alloy, the melt was stirred with a mechanical stirrer at 150rpm for 5 minutes. Thereafter, the melt was allowed to settle for 15 minutes and a 30mm thick plate sample (160mm x 140mm) was then sand cast at 730°C. A plate sample of the pure magnesium was also sand cast at 730°C prior to addition of the master alloy. The pure magnesium plate sample had an average grain size of approximately 10,000µm. After alloying with the master alloy the resultant plate sample had an average grain size of 98µm, a soluble zirconium content of 0.49% and a total zirconium content of 0.58%.

It is to be understood that where the word "comprise", and variations such as "comprises" and "comprising", are used in this specification, unless the context requires otherwise such use is intended to imply the inclusion of a stated feature or features but is not to be taken as excluding the presence of other feature or features.

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The reference to any prior art in this specification is not, and should not be taken as, an acknowledgment or any form of suggestion that such prior art forms part of the
5 common general knowledge in Australia or elsewhere.

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CLAIMS

1. A method for treating zirconium metal, the method comprising chemically depassivating the zirconium metal.
2. A method for treating zirconium sponge, the method comprising chemically depassivating the zirconium sponge to form treated zirconium sponge.
3. A method as claimed in claim 2 wherein the zirconium sponge is chemically depassivated by treatment with a source of fluoride ions.
4. A method as claimed in claim 3 wherein the source of fluoride ions is an acidified solution containing fluoride ions.
5. A method as claimed in claim 3 wherein the source of fluoride ions is hydrofluoric acid.
6. A method for treating zirconium sponge, the method comprising treating the zirconium sponge with a solution containing fluoride ions to form treated zirconium sponge.
7. Treated zirconium sponge prepared by a method as claimed in any one of claims 2-6.
8. Zirconium sponge comprising an agglomerate of zirconium particles and having a surface layer containing fluorine containing compounds at least partially coating at least some of the particles.
9. Zirconium sponge as claimed in claim 8 wherein the fluorine containing compounds are zirconium fluoride compounds.
10. Zirconium sponge as claimed in claim 9 wherein the zirconium fluoride compounds have the formula $Zr_xF_y \cdot nH_2O$.
11. A method of manufacturing a magnesium-zirconium master alloy, the method comprising the steps of:
 - (a) mixing treated zirconium sponge as claimed in claim 7 or zirconium sponge as claimed in any one

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- of claims 8-10 with molten magnesium/magnesium alloy to form a magnesium-zirconium melt containing dissolved zirconium and zirconium particles; and
- 5 (b) casting the magnesium-zirconium melt to solidify as the magnesium-zirconium master alloy.
12. A magnesium-zirconium master alloy manufactured by a method as claimed in claim 11.
- 10 13. A magnesium-zirconium master alloy as claimed in claim 12 containing 10-50% by weight zirconium.
14. A magnesium-zirconium master alloy as claimed in claim 12 containing 20-40% by weight zirconium.
- 15 15. A magnesium-zirconium master alloy as claimed in any one of claims 12-14 wherein 90% of the zirconium particles are sized less than 5 μ m.
16. A magnesium-zirconium master alloy containing dissolved zirconium and zirconium particles in the substantial absence of halide inclusions, wherein 90% of the zirconium particles are sized less than 5 μ m.
- 20 17. A magnesium-zirconium master alloy as claimed in claim 15 or claim 16 wherein 90% of the zirconium particles are sized less than 3 μ m.
18. A method of adding zirconium as an alloying element to molten magnesium/magnesium alloy, the method comprising mixing treated zirconium sponge as claimed in claim 7 or zirconium sponge as claimed in any one of claims 8-10 with the molten magnesium/magnesium alloy.
- 25 19. A method of adding zirconium as an alloying element to molten magnesium/magnesium alloy, the method comprising mixing a magnesium-zirconium master alloy as claimed in any one of claims 12-17 with the molten magnesium/magnesium alloy.
- 30 20. A magnesium alloy containing zirconium prepared by a method as claimed in claim 18 or claim 19.

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FIG. 1

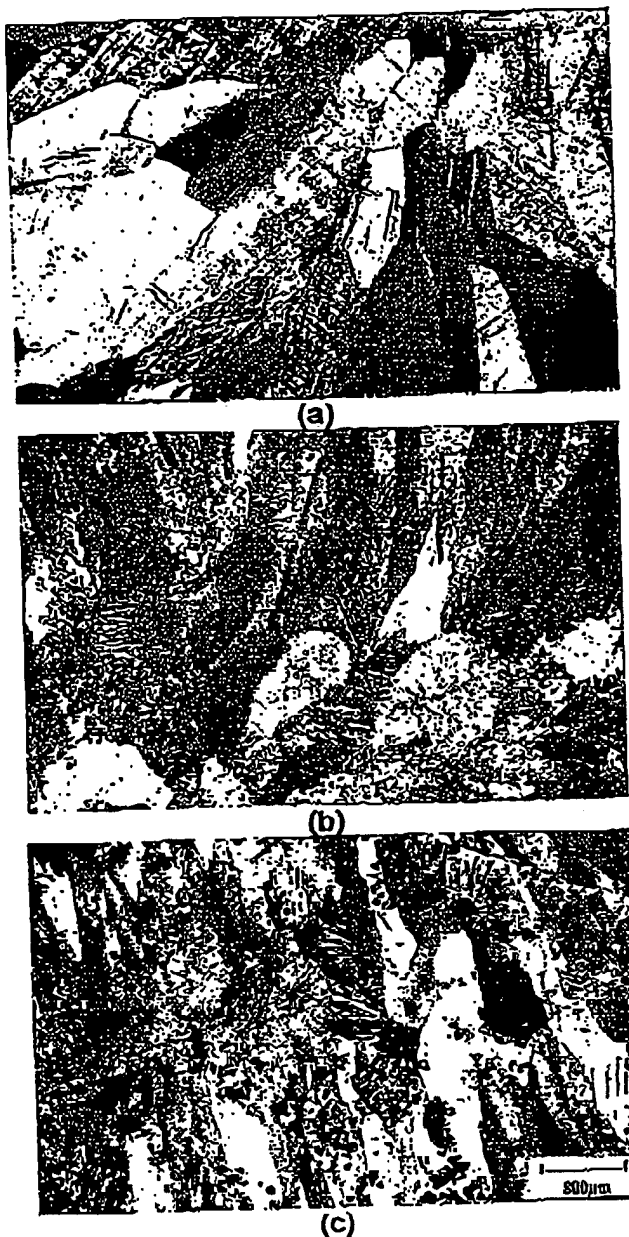


Figure 1 Optical micrographs showing the grain refining ability of as-received sponge when added to pure magnesium at 730 °C. All micrographs are of the same magnification. (a) Pure magnesium, (b) after adding 1% sponge, followed by 30 minutes manual stirring, and (c) adding a further 1% sponge and applying 30 minutes manual stirring.

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FIG 2

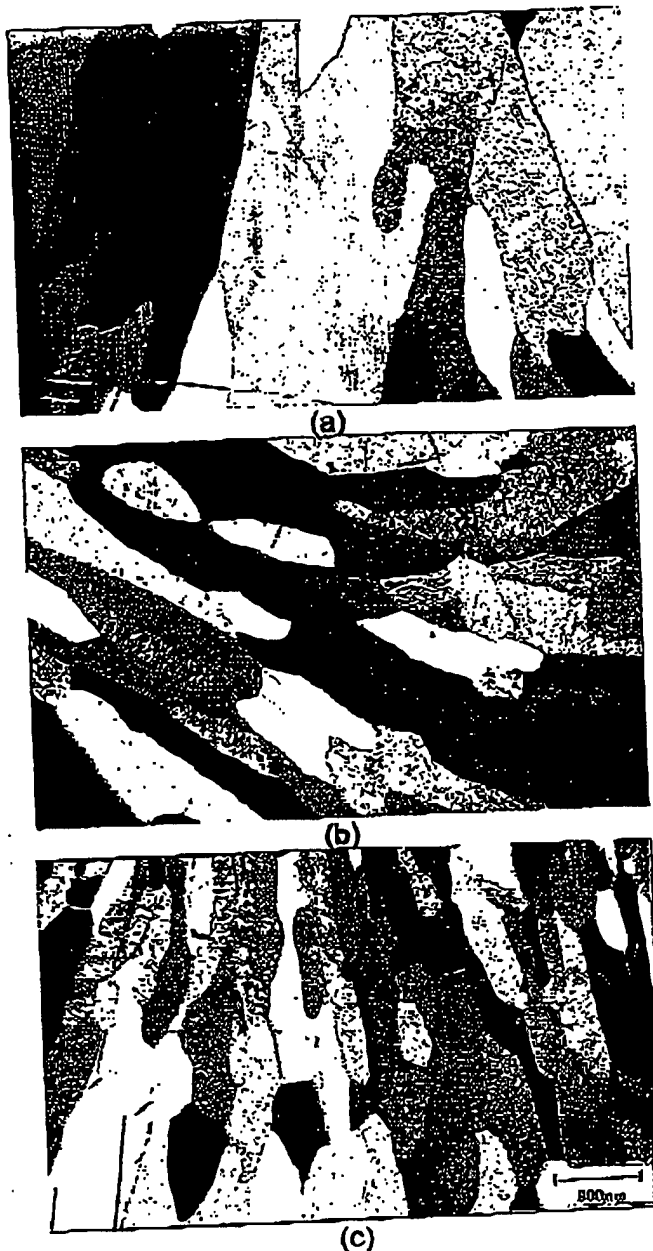


Figure 2 Optical micrographs showing the grain refining ability of as-received sponge when added to pure magnesium at 780 °C. All micrographs are of the same magnification. (a) Pure magnesium, (b) after adding 1% sponge, followed by two minutes manual stirring and then 30 minutes holding at temperature, and (c) a further holding of 210 minutes at temperature.

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FIG 3

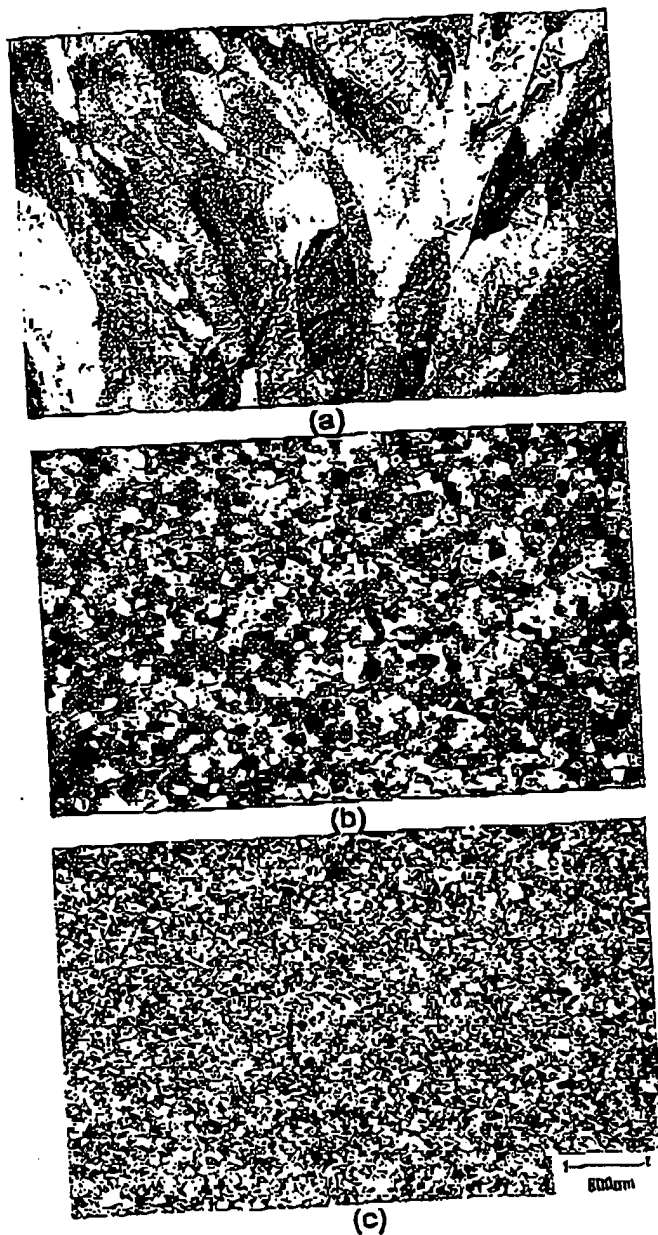


Figure 3 Optical micrographs showing the grain refining ability of pretreated sponge when added to pure magnesium at 680 °C. All micrographs are of the same magnification. (a) Pure magnesium, (b) after adding 1 wt% sponge, followed by 20 minutes manual stirring, and (c) after a further 10 minutes stirring.

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FIG 4

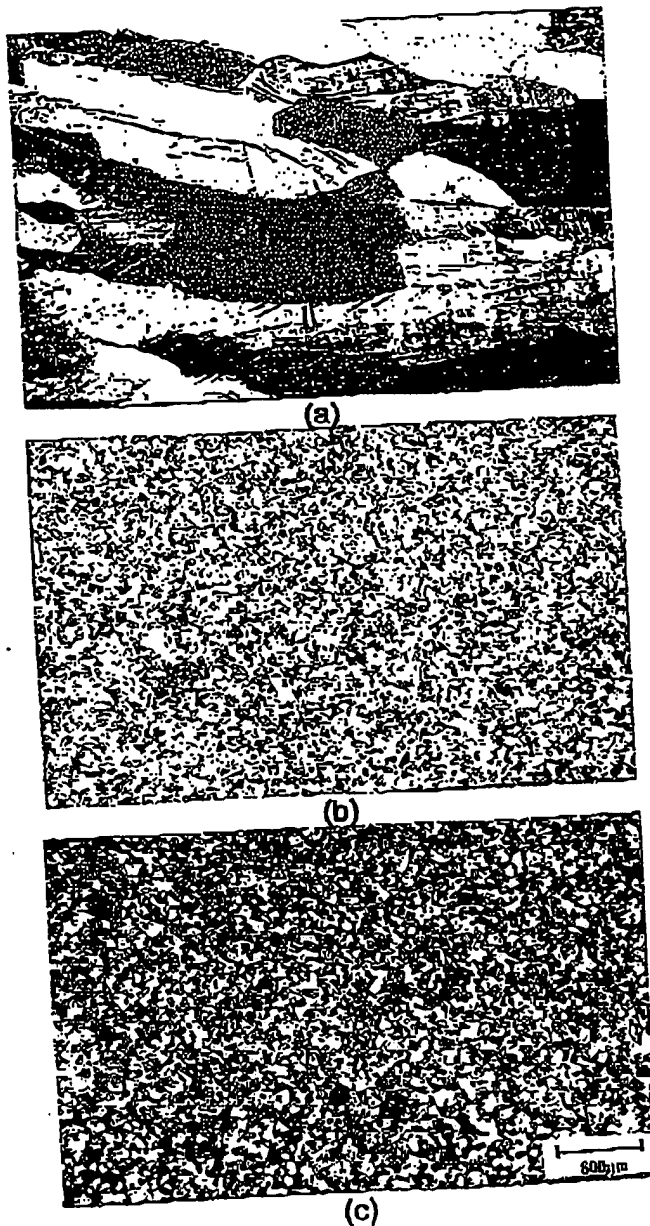


Figure 4 Optical micrographs showing the grain refining ability of pretreated sponge when added to pure magnesium at 730 °C. All micrographs are of the same magnification. (a) Pure magnesium, (b) after adding 1 wt% sponge, followed by 30 minutes manual stirring, and (c) after 30 minutes of holding following (b) and then restirring the melt for two minutes.

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FIG 5

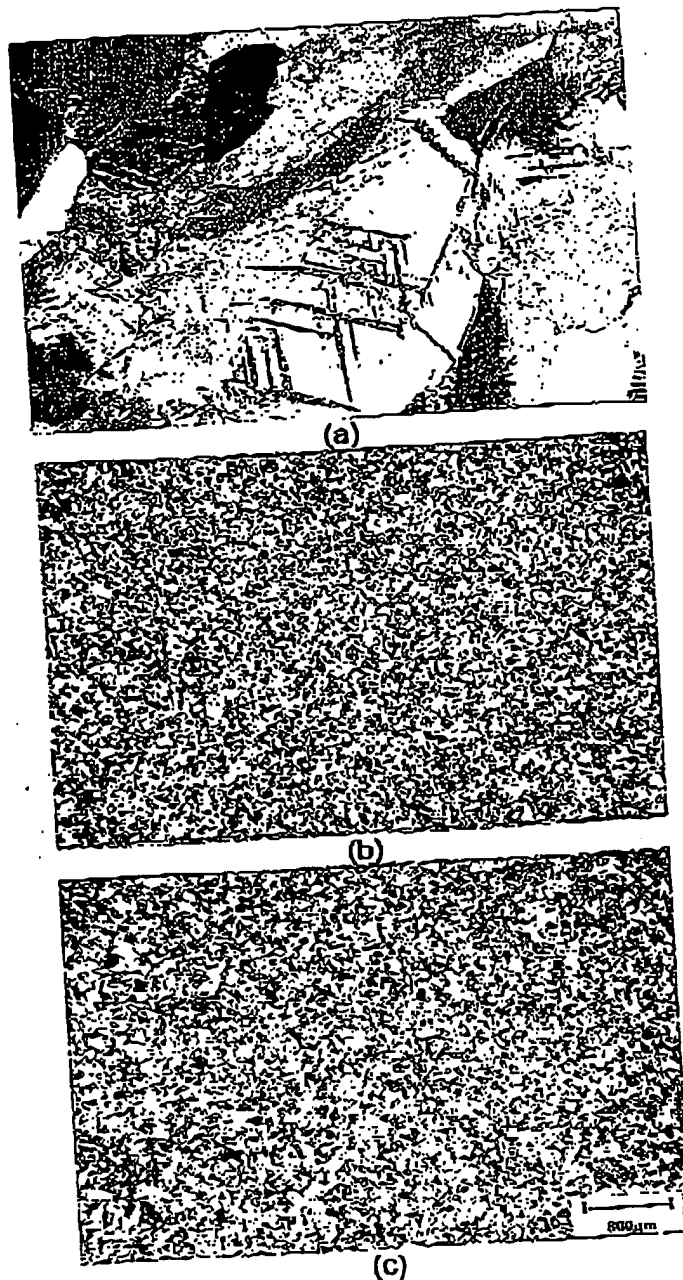


Figure 5 Optical micrographs showing the grain refining ability of pretreated sponge when added to pure magnesium at 800 °C. All micrographs are of the same magnification. (a) Pure magnesium, (b) after adding 1 wt% sponge, followed by 30 minutes manual stirring, and (c) after 30 minutes of holding following (b) and then restirring the melt for two minutes.

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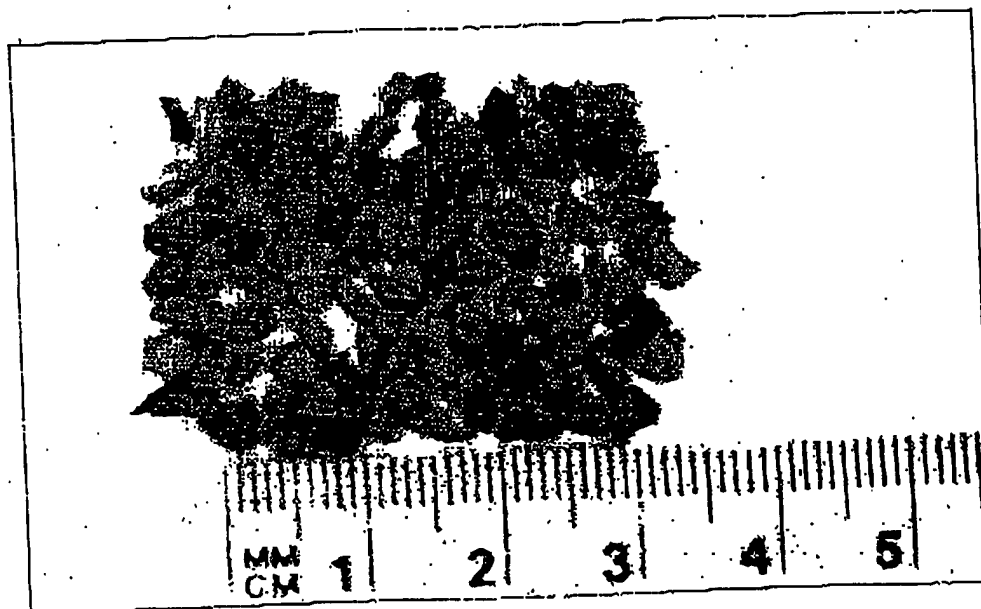


Fig. 6

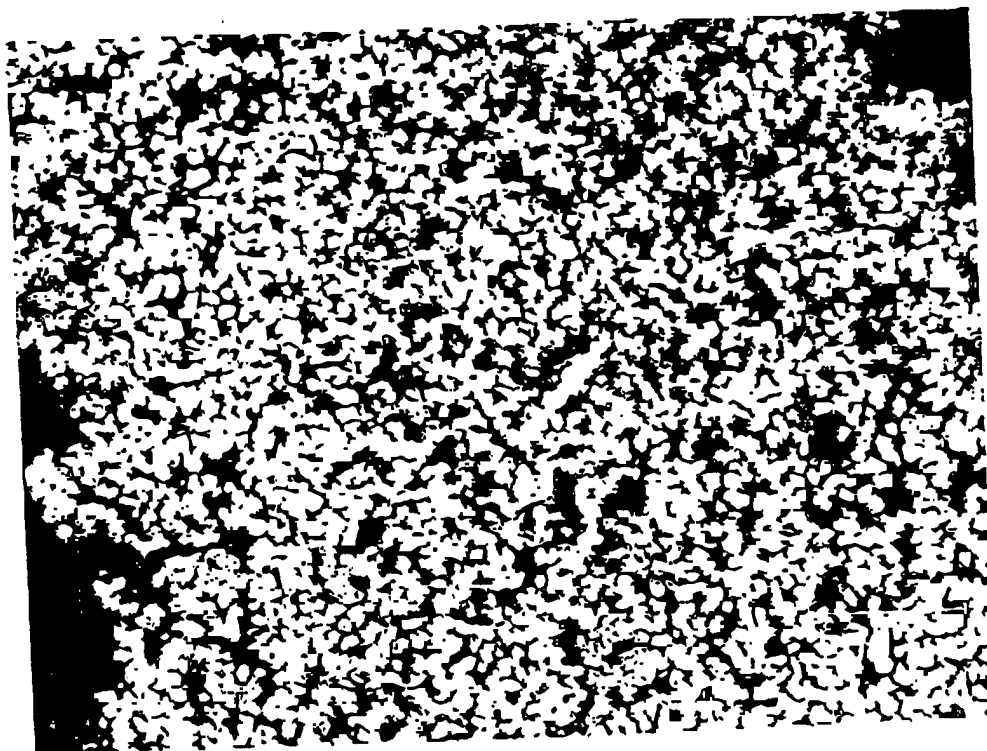


Fig. 7

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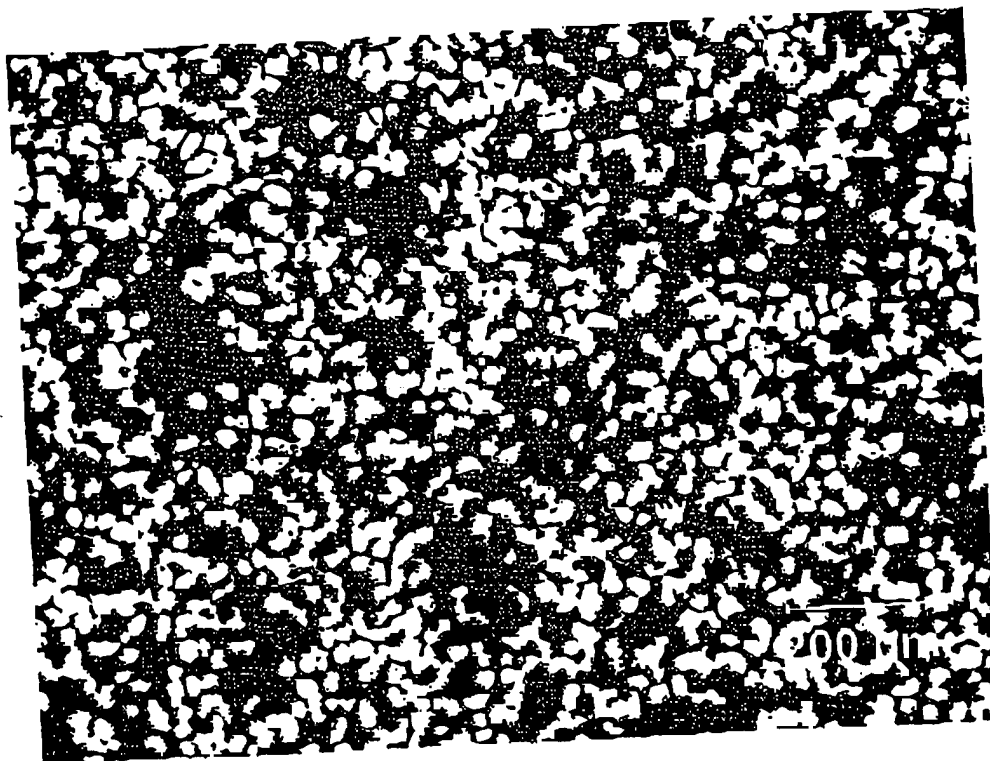


Fig. 8

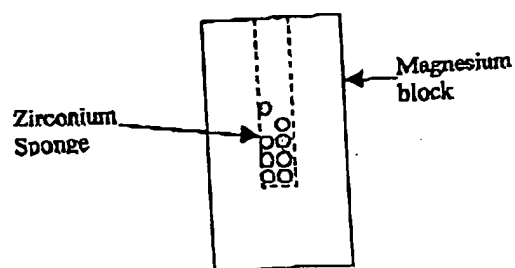
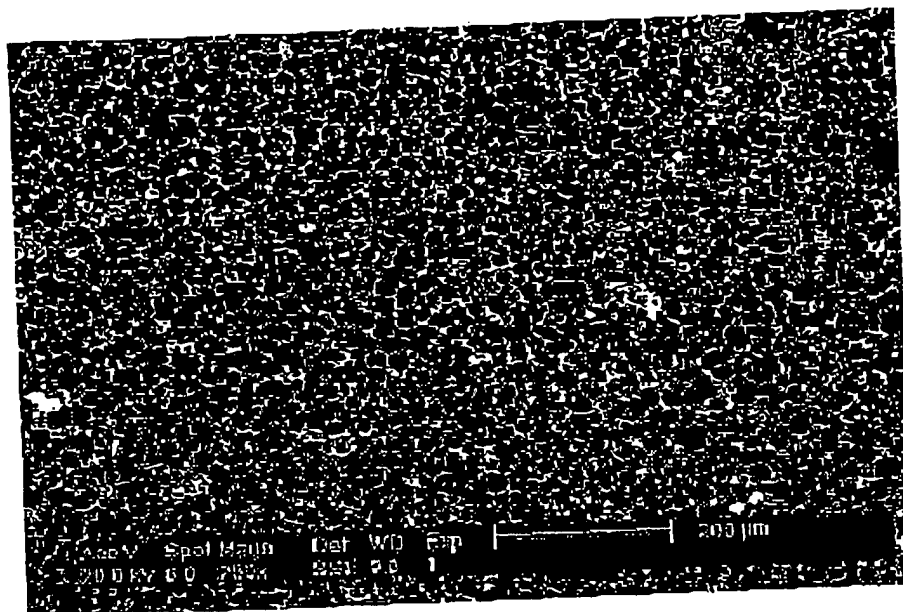
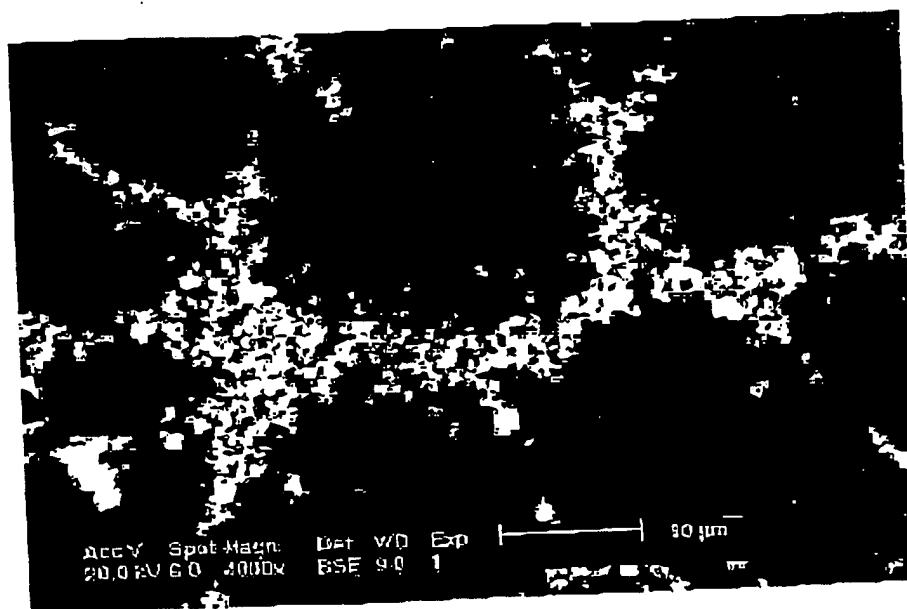


Fig. 9

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**Fig. 10****Fig. 11**

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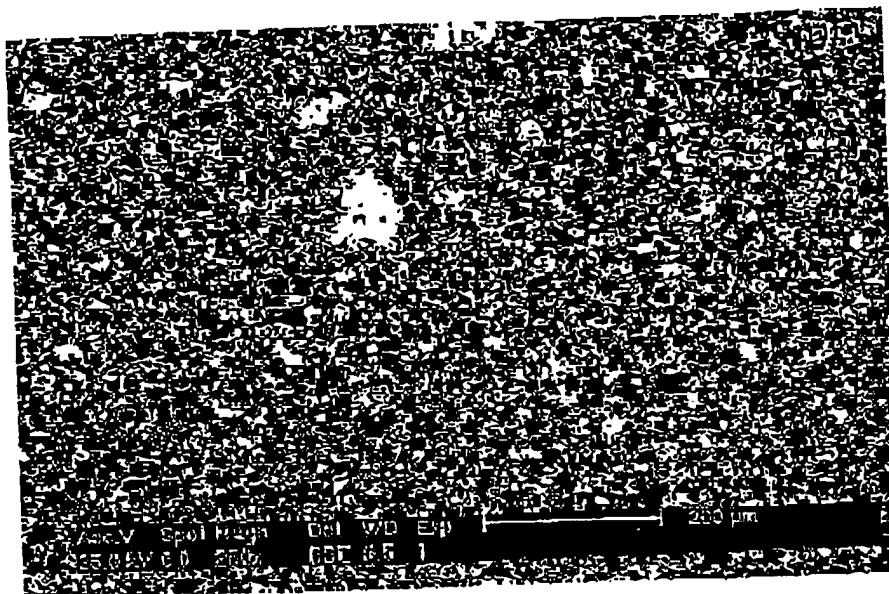


Fig. 12

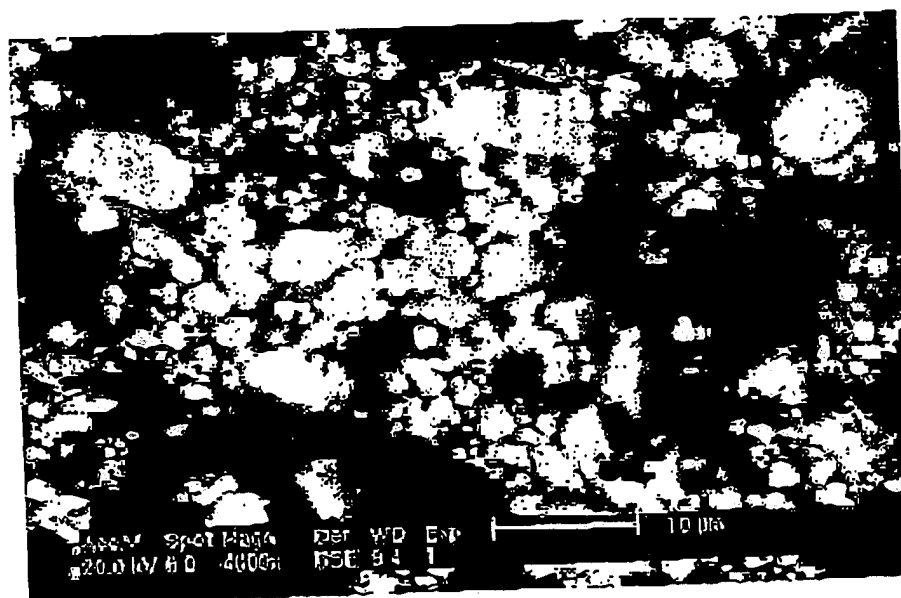


Fig. 13

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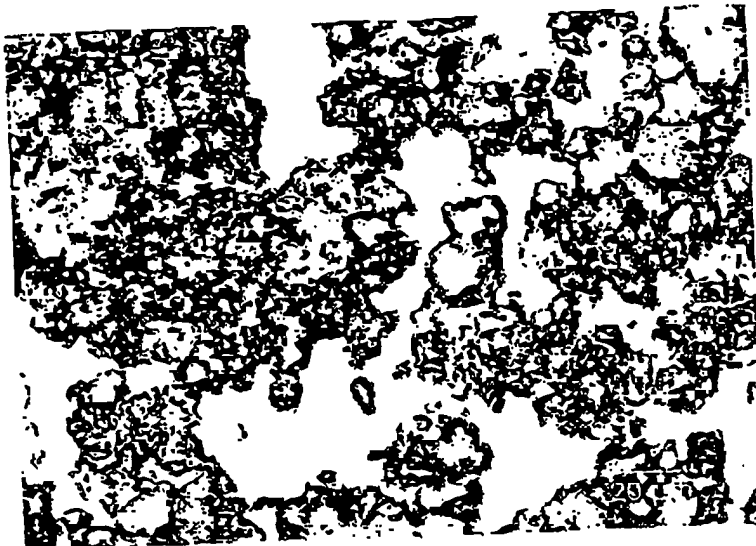


Fig. 14

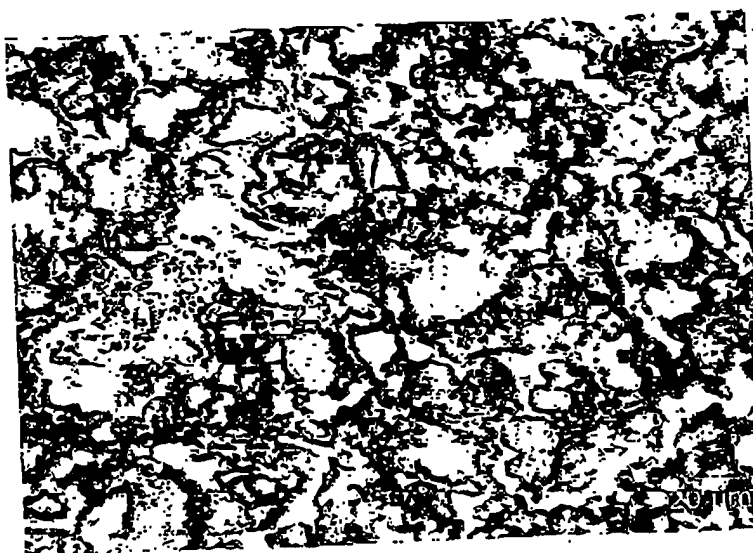


Fig. 15

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU03/00053**A. CLASSIFICATION OF SUBJECT MATTER**Int. Cl. ⁷: C23F 3/06, C23G 1/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHEDMinimum documentation searched (classification system followed by classification symbols)
IPC⁷ AS ABOVE

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Derwent WPI: IPC⁷ as above and +Fluor+ and +passivat+ and hydrofluoric acid**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	Derwent Abstract Accession No. 38983X/21 Class M12. JP 51-041639 (Kobe Steel KK) 8 April 1976 Abstract	1 - 7, 11 - 15, 18 - 20
A	Derwent Abstract Accession No. 84-289020/47, Class M12, DD 211811 A (Veb Galvanotech Lei) 25 July 1984 Abstract	1 - 7, 11 - 15, 18 - 20

☐ Further documents are listed in the continuation of Box C☒ See patent family annex

- * Special categories of cited documents:
- "A" document defining the general state of the art which is not considered to be of particular relevance
 - "E" earlier application or patent but published on or after the international filing date
 - "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
 - "O" document referring to an oral disclosure, use, exhibition or other means
 - "P" document published prior to the international filing date but later than the priority date claimed
 - "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
 - "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
 - "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
 - "Z" document member of the same patent family

Date of the actual completion of the international search
4 April 2003

Date of mailing of the international search report 14 APR 2003

Name and mailing address of the ISA/AU
AUSTRALIAN PATENT OFFICE
PO BOX 200, WODEN ACT 2806, AUSTRALIA
E-mail address: pct@ipaustralia.gov.au
Facsimile No. (02) 6285 3929

Authorized officer

DAVID K. BELL

Telephone No : (02) 6283 2309

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU03/00053**Box I** Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos :
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos :
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos :
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a)

Box II Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

See Supplementary Sheet.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
Claims 1 to 7, 11 to 15 and 18 to 20

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU03/00053**Supplemental Box**

(To be used when the space in any of Boxes I to VIII is not sufficient)

Continuation of Box No: II

Claims 1 to 7, 11 to 15 and 18 to 20 are directed to a method of treating zirconium metal (or sponge) to depassivate the metal.

Claims 8 to 10 are directed to a zirconium sponge consisting of an agglomerate of zirconium particles having a surface layer containing fluorine containing compounds.

Claim 16 is directed to a magnesium - zirconium master alloy having a zirconium particle size of 90% less than 5 μ m.

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/AU03/00053

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited In Search Report		Patent Family Member
JP	51041639	NONE
OD	211811	DE 3009778
		END OF ANNEX

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